ARTICLE

# Synthesis and Characterization of Fluorinated Polyurethane Containing Carborane in the Main Chain: Thermal, Mechanical and Chemical Resistance Properties

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**Abstract** In this study, two fluorinated polyurethanes (FPU) containing carborane groups in the main chains were firstly designed and synthesized *via* the reaction of hexamethylene diisocyanate trimer (HDI trimer) with fluorinated polyesters (CFPETs) having hydroxyl-terminated carborane groups at room temperature. The structures of carborane fluorinated polyesters (CFPETs) and polyurethanes (CFPUs) were characterized by gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) measurements. The thermal stability, mechanical properties, Shore A hardness, solvent resistance and acid-alkali resistance of the carborane fluorinated polyurethane films were also studied. Thermogravimetric analysis (TGA) tests manifested that the introduction of carborane groups into the main chain of fluorinated polyurethane endowed the obtained fluorinated polyurethane with excellent thermal stability. The thermal decomposition temperature of carborane fluorinated polyurethane (CFPU) increased by 190 °C compared with that of the carborane-free fluorinated polyurethane (FPU). Even at 800 °C, CFPU showed the char yield of 66.5%, which was higher than that of FPU (34.3%). The carborane-containing fluorinated polyurethanes also showed excellent chemical resistance and prominent mechanical property even after the cured films being immersed into Jet aircraft oil or 37% HCl for 168 h or at high temperature (700 °C). It is found that the structural characteristics of carborane group and the compacted structure of CFPU effectively improve the thermal stability, mechanical property, solvent resistance and acid-alkali resistance of the carborane-free fluorinated polyurethane. These excellent properties make CFPU as the useful raw materials to prepare the high temperature resistant coatings or adhesives for automotive engines, engine or fuel tank of aircraft and other equipment working in high-temperature or high concentrations of acid-alkali environments.

**Keywords** Fluorinated polyurethane; Carborane; Thermal stability; Mechanical property; Chemical resistance

## INTRODUCTION

Fluorinated polyurethane (FPU)[1, 2] is a new class of functional materials synthesized by incorporating fluorocarbon chains into the molecular chains of polyurethane (PU)[3−5]. They possess many outstanding properties, such as high thermal stability and chemical resistance (to acids, alkalis and solvents), good mechanical property, and attractive surface properties[2, 6−12]. In this regard, FPUs have great application prospects in the areas of protective coatings, paint industry, leather decoration and medicine[13−17]. In recent years, the study of fluorinated polyurethane has attracted considerable interest. As known, the main drawback of FPUs is that they cannot bear harsh environment, such as extremely high temperature and high concentration of acid-alkali corrosion. However, such

properties are exactly required in the high-tech fields such as aerospace, aviation and military industry, *etc*. Hence, it is important to further improve the thermal stability and acid-alkali resistance of FPUs. One adopted approach for the improvement of thermal stability of polyurethanes is the structure modification by introducing organic heterocyclic groups into the main chains of polymeric diols and PUs, such as isocyanurates, oxazolidone, imide, *etc*. The effect of different organic heterocyclic groups on improving the thermal performance of polyurethanes has been reported[18−23], but the most working temperature ranges of these polymers are still lower than 500 °C. In addition, under the high temperature and acid-alkali conditions, the mechanical property of these polymers is unsatisfactory. Up to now, to find a more stable group with FPUs for achieving the requirements of extremely high thermal stability, solvent resistance and mechanical property is still a challenge.

Carborane ($C_2B_{10}H_{12}$) is a good candidate for improving the properties of FPUs. Carborane is a stable icosahedral

molecule with two carbon atoms and ten boron atoms, which has three isomers: 1,2-carborane, 1,7-carborane, and 1,12-carborane. The icosahedral geometry and rich boron content endow carborane with several unusual properties, especially thermal property. In addition, the "super aromatic" cage structure, a role of "energy groove", and the strong electron-deficiency make the molecule stable and the corresponding polymer more compact. Meanwhile, the large size of the cage structure has strong steric effect on the adjacent groups, leading to excellent chemical stability[24–27]. Owing to these distinctive properties, carborane has been regarded as one of the most excellent organic groups to improve the performance of organic polymers with remarkable thermal and chemical stability, such as polyesters, polysilanes, polysiloxanes and polybenzoxazines[28–35]. Predictably, incorporating carborane groups into the molecular chains of FPUs may be an effective approach to improve the thermal and chemical stability of FPUs. To the best of our knowledge, these kinds of carborane-containing FPUs have not been reported yet so far.

Herein, we designed and synthesized two new carborane-containing FPUs (CFPU-1 and CFPU-2). CFPU-1 and CFPU-2 were synthesized *via* two steps. Firstly, carborane groups were introduced into the main chain of

fluorinated polyester to obtain the hydroxyl-terminated carborane-containing fluorinated polyesters (CFPETs) by reacting "HOOC-VDF-*co*-HFP-COOH" with carborane diols (CDO-1 and CDO-2). The "HOOC-VDF-*co*-HFP-COOH" is a kind of carboxyl terminated liquid fluorine elastomer (LFE) prepared in our laboratory. Secondly, the CFPETs reacted with hexamethylene diisocyanate trimer (HDI trimer) to obtain the final product of carborane-containing fluorinated polyurethanes (CFPUs). The synthesis routes of carborane-containing fluorinated polyesters (CFPET-1 and CFPET-2) and the corresponding carborane-containing FPUs (CFPU-1 and CFPU-2) are shown in Scheme 1. The obtained CFPETs and CFPUs were characterized by gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, and ¹H-nuclear magnetic resonance (¹H-NMR) measurements. The thermal stability, resistance of the CFPU films were also measured. The results indicated that CFPUs exhibited improved thermal stability and higher acid-alkali resistance as compared with the carborane-free FPU (FPU-1). Even at high temperature or acid-alkali environment, the carborane-containing CFPUs also showed good mechanical properties superior to the carborane-free FPU. We believe the carborane-containing fluorinated polyurethanes can be widely used as the raw materials to prepare the high
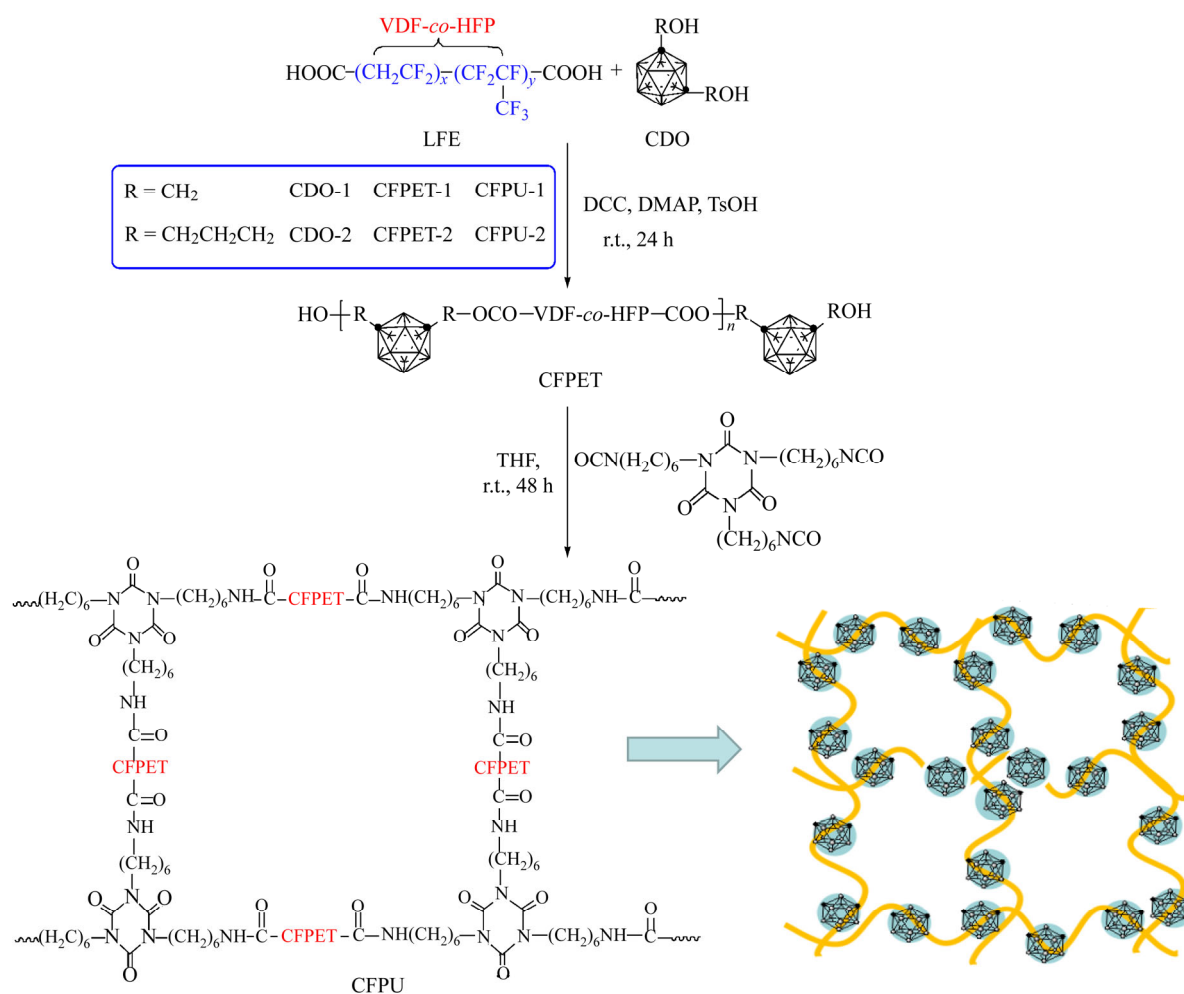


**Scheme 1**    The synthetic routes of carborane-containing fluorinated polyesters (CFPET-1 and CFPET-2) and carborane-containing fluorinated polyurethanes (CFPU-1 and CFPU-2)

temperature resistant coatings, sealant or adhesives for automotive engines, engine or fuel tank of aircraft and other equipment working in high-temperature or high concentrations of acid-alkali environments. Under these harsh environments, the good thermal stability, excellent chemical resistance and mechanical properties of carborane-containing fluorinated polyurethanes are capable of keeping fluorinated polyurethane stable and expanding their service lives.

## EXPERIMENTAL

### Materials

Carboxyl terminated liquid fluorine elastomer (LFE) was synthesized and purified according to the previously described synthetic route in the literature[36] ($M_w$ = 2600, $M_w/M_n$ = 1.88). Carborane diols (1,7-bis-(hydroxymethyl)-carborane (CDO-1) and 1,7-bis-(hydroxypropyl)-carborane (CDO-2)) were prepared with the same procedures reported in the previous papers[37]. *N,N′*-dicyclohexyl-carbodiimide (DCC) was obtained from GuoYao Chemical Group Co., Ltd. 4-Dimethylaminopyridine (DMAP) and dibutyltin dilaurate (DBTDL) were supplied by Aladdin. *p*-Toluenesulfonic acid (TsOH) was provided by Xilong Chemical Co., Ltd. HDI trimer was purchased from Bayer Chemical Group Co., Ltd. Acetone, ethyl acetate, tetrahydrofuran (THF), Jet aircraft oil, cyclohexane were purchased from Beijing Chemical Group Co., Ltd. Hydrochloric acid and sodium hydroxide were purchased from Tianjin Chemical Group Co., Ltd. All the chemicals were used as received without any further purification.

### Instrumentation

FTIR spectra were measured by a Nicolet Nexus 670 FTIR spectrophotometer with a scanning range from 4000 cm$^{-1}$ to 400 cm$^{-1}$. $^1$H-NMR spectra were recorded using a Bruker AV400 spectrometer with acetone-d$_6$ and deuterated chloroform (CDCl$_3$) as the solvents, and tetramethylsilane (TMS; $\delta$ = 0 ppm) was used as an internal standard. Molecular weight ($M_w$) and polydispersity ($M_w/M_n$) of the polymers were tested in THF by a Waters 515 gel permeation chromatography (GPC) system. The thermogravimetric analysis (TGA) was performed on a TA SDT-Q600 thermogravimetric analyzer from 50 °C to 800 °C under air atmosphere at a fixed heating rate of 10 K/min. Heat release rate (HRR) and total heat release (THR) were tested as the standard ISO 5660-1-2002 using the JCZ-2 cone calorimeter (Nanjing Jiangning Analytical Instruments Co., Ltd.); thermal radiation flux was 50 kW/m$^2$. Limited oxygen index (LOI) was studied as the national standard GB-T 10707-2008 using JF-3 Oxygen Index Testing Apparatus (Beijing Beiguang Jingyi Instruments Co., Ltd.). Tensile strength and elongation at break were tested as a Chinese National Standard (GB/T 528-2009) using a RGT-5 electronic universal testing machine manufactured by Shenzhen Reger Instrument Co., Ltd. Hardness was tested by Shore Hardness tester using Chinese National Standard (GB531-1999). Impact strength was tested as Chinese National Standard (GB/T 2567-2008) using the HIT-2492 impact testing machine. The static contact angle of cured FPU films was measured by the sessile drop method at 25 °C using a Cam 200 optical contact angle meter (Dataphysics Instruments Co., Ltd.). Distilled water and ethylene glycol were used in the measurement. Typically, five angle measurements were made and the data were averaged. Chemical resistance of cured CFPU film was characterized according to ASTM D471-02. The cured CFPU films were immersed in the media (Jet aircraft oil, cyclohexane, 37% HCl and 45% NaOH, respectively) at room temperature for 168 h. The weight change of the films was calculated by using the following Eq. (1):

$$\text{Weight change (\%)} = [(W_2 - W_1)/W_1] \times 100 \qquad (1)$$

where $W_1$ and $W_2$ represent the film weights before and after immersed into the media, respectively.

### Synthesis of Carborane-containing Fluorinated Polyesters (CFPETs)

The synthetic routes of carborane-containing fluorinated polyesters (CFPETs) and carborane-containing FPUs (CFPUs) are shown in Scheme 1. The carborane-containing hydroxyl-terminated fluorinated polyesters (CFPET-1 and CFPET-2) were synthesized *via* Steglich esterification by reacting carboxyl terminated liquid fluorine elastomer (LFE) with corresponding carborane diols (CDO-1 and CDO-2), respectively. The carborane-free fluorinated polyester (FPET-1) was synthesized from carboxyl terminated liquid fluorine elastomer and ethylene glycol by the same procedure.

*Synthesis of CFPET-1*

In a 250 mL one-necked round bottom flask, carboxyl terminated liquid fluorine elastomer (LFE, 6.27 g, 2.03 mmol), 1,7-bis-(hydroxymethyl)-carborane (CDO-1, 0.40 g, 2.03 mmol), DCC (0.56 g, 3.01 mmol), DMAP (0.02 g, 0.21 mmol), TsOH (0.02 g, 0.12 mmol) were dissolved in THF (50 mL) and stirred for 48 h at 25 °C. Then 1,7-bis-(hydroxymethyl)-carborane (CDO-1, 0.03 g, 0.08 mmol) was added into the mixture, and the mixture was stirred for another 2 h. After filtering, the solvent was removed by reduced pressure distillation again. The obtained viscous residue was purified by column chromatography on silica gel by using a mixed eluent of petroleum ether and ethyl acetate (10/1, *V/V*). A brown solid (71%) was obtained as the target product, m.p. 160 °C. GPC: $M_w$ = 1.25 × 10$^4$, PDI = 1.93. The amount of carborane is 5.02%. FTIR ($\nu$, cm$^{-1}$, KBr): 3375 (−OH), 2996, 3034 (−CH$_2$−), 2600 (BH), 1720 (C=O), 1600−1680 (C=C), 1396 (−FCH$_2$), 1204 (−CF$_2$−), 886 (−CF$_3$), 720 (C−C). $^1$H-NMR (400 MHz, $\delta$, ppm): 3.64 (s, COO−CH$_2$−), 3.49 (s, O−CH$_2$−), 2.74−3.41 and 3.31−2.65 (m, −CH$_2$CF$_2$−), 3.41−0.81 (m, B−H).

*Synthesis of CFPET-2*

CFPET-2 was synthesized from 1,7-bis-(hydroxypropyl)-carborane (CDO-2) by the procedure similar to that used for preparation of CFPET-1. A brown solid with a yield of 72% and m.p. 187 °C was obtained as the target product. $M_w$ = 1.31 × 10$^4$, PDI = 2.06. The amount of carborane is 4.90%. FTIR ($\nu$, cm$^{-1}$, KBr): 3373 (−OH), 2908 (−CH$_2$−), 2601 (BH), 1723 (C=O), 1600−1680 (C=C), 1397 (−FCH$_2$), 1204 (−CF$_2$−), 886 (−CF$_3$), 720 (C−C). $^1$H-NMR

(400 MHz, $\delta$, ppm): 3.49 (s, O—CH$_2$—), 3.64 (t, COO—CH$_2$—), 2.74–3.41 and 3.31–2.65 (m, —CH$_2$CF$_2$—), 3.42–0.90 (m, B—H,), 3.83, 3.62, 2.10, 1.92 and 1.79 (m, —CH$_2$CH$_2$—), 1.42 (s, OH).

### Synthesis of Carborane-free Fluorinated Polyester (FPET-1)

FPET-1 was synthesized from carboxyl terminated liquid fluorine elastomer and ethylene glycol by the procedure similar to that used for preparation of CFPET-1. A rich yellow solid with a yield of 78% and m.p. 154 °C was obtained as the target product. $M_w = 1.44 \times 10^4$, PDI = 1.75. FTIR ($\nu$, cm$^{-1}$, KBr): 3373 (—OH), 2910 (—CH$_2$—), 1723 (C=O), 1600–1680 (C=C), 1398 (—FCH$_2$), 1205 (—CF$_2$—), 886 (—CF$_3$), 720 (C—C). $^1$H-NMR (400 MHz, $\delta$, ppm): 4.71 (s, —C(CF$_3$)=CH—), 4.15–2.74 (m, —CH$_2$CF$_2$—), 1.82 (CH$_2$), 1.32 (OH).

### Synthesis of Carborane-containing Fluorinated Polyurethans (CFPU-1 and CFPU-2)

The carborane-containing CFPUs were prepared *via* a single-step by employing CFPETs and HDI trimer with the molar ratio of NCO/OH = 1/1.5. 5.0 g of CFPET-1 was dissolved into 50 mL of THF solution, and then HDI trimer and DBTDL (0.4 wt%) were added into the solution. After stirring for 2 h at 80 °C under air, the mixture was poured onto the treated mold and put horizontally at room temperature. After 72 h, the product CFPU-1 was obtained as a rich yellow translucent membrane-like substance. The amount of carborane is 4.71%. FTIR ($\nu$, cm$^{-1}$, KBr): 3350 (—NH), 2601 (—BH), 1687 (C=O), 1205 (—C—O—C—), 1400 (—FCH$_2$), 882 (—CF$_3$). At the same time, CFPU-2 was prepared from CFPET-2 and HDI trimer. The amount of carborane is 4.69%. CFPU-2 FTIR ($\nu$, cm$^{-1}$, KBr): 3350 (—NH), 2595 (—BH), 1710 (C=O), 1209 (—C—O—C—), 1401 (—FCH$_2$), 885 (—CF$_3$).

### Synthesis of Carborane-free Fluorinated Polyurethanes (FPU-1)

FPU-1 was prepared *via* the reaction of FPET-1 and HDI trimer with the molar ratio of NCO/OH = 1/1.5. The procedure is similar to that used for preparation of CFPU-1. FTIR ($\nu$, cm$^{-1}$, KBr): 3350 (—NH), 1687 (C=O), 1205 (—C—O—C—), 1400 (—FCH$_2$), 882 (—CF$_3$).

## RESULTS AND DISCUSSION

### Characterization of Carborane-containing Fluorinated Polyesters (CFPET-1 and CFPET-2)

Carborane-containing fluorinated polyesters (CFPET-1 and CFPET-2) were synthesized *via* the Steglich esterification of carboxyl terminated liquid fluorine elastomer (LFE) with corresponding carborane diols (CDO-1 and CDO-2) according to the synthetic routes shown in Scheme 1. Dicyclohexylcarbodiimide (DCC) and 4-dimethylamino pyridine (DMAP) were used as the dehydrating agent and the catalyst, respectively. For the subsequent synthesis of polyurethanes, the terminal hydroxyl groups of polyesters were needed, so after carboxyl terminated liquid fluorine elastomer (LFE) reacted with carborane diols in the molar

ratio of 1/1, another 0.08 mmol of carborane diol was added into the reaction system. Finally, the carborane-containing hydroxyl-terminated fluorinated polyester was obtained. The terminated hydroxyl groups could further react with HDI trimer to form CFPUs. The yield and molecular weight ($M_w$) of the fluorinated polyesters are listed in Table 1.

**Table 1** Yield and molecular weight ($M_w$) of the carborane-containing fluorinated polyesters (CFPET-1 and CFPET-2) and the carborane-free fluorinated polyester FPET-1

| No. | Polymer | Yield (%) | $M_w$ [a] | $M_w/M_n$ [a] |
|-----|---------|-----------|-----------|---------------|
| 1 | LFE | – | $0.26 \times 10^4$ | 1.88 |
| 2 | CFPET-1 | 71 | $1.25 \times 10^4$ | 1.93 |
| 3 | CFPET-2 | 72 | $1.31 \times 10^4$ | 2.06 |
| 4 | FPET-1 | 78 | $1.44 \times 10^4$ | 1.75 |

[a] Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration.

The chemical structures of synthesized fluorinated polyesters (CFPET-1, CFPET-2 and FPET-1) were well characterized with spectroscopic methods. The FTIR spectra of fluorinated polyesters (CFPET-1, CFPET-2 and FPET-1) are shown in Fig. 1. The spectra of the carboxyl terminated liquid fluorine elastomer (LFE) and carborane diols (CDO-1 and CDO-2) are also given in Fig. 1 for comparison. The strong absorption peaks at 886, 1204, and 1396 cm$^{-1}$ are ascribed to the stretching vibration of —CF$_3$, —CF$_2$— and —CH$_2$F respectively, which exist both in the FTIR spectra of the liquid fluorine elastomer LFE and fluorinated polyester FPET-1, CFPET-1 and CFPET-2. It clearly indicates that the fluorinated polyesters have the same backbone structure as LFE. Besides, in the FTIR spectra of carborane diols (CDO-1 and CDO-2) and fluorinated polyester (CFPET-1 and CFPET-2), the absorption peak at 2600 cm$^{-1}$ is ascribed to the stretching vibration of B—H bonds on the carborane cage. This result indicates that the carborane groups have been introduced into the fluorinated polyester. Moreover, the intensity of the absorption band around 3375 cm$^{-1}$ becomes weaker, which further confirms that carborane diol has been incorporated into the polyester terminated with the hydroxyl groups. Expect for these peaks, a new peak at 1720 or
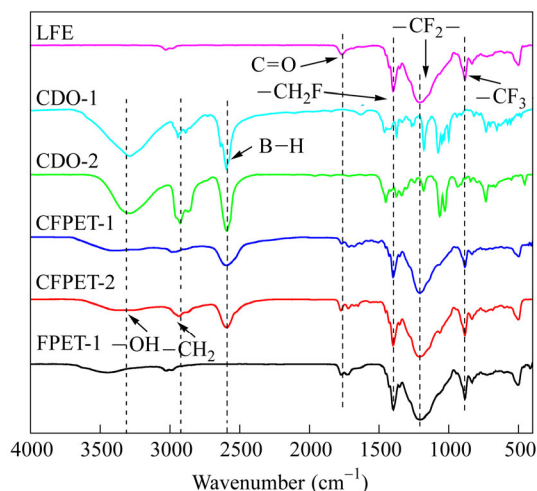


**Fig. 1** FTIR spectra of the reactants (LFE, CDO-1 and CDO-2) and the polyesters (CFPET-1, CFPET-2 and FPET-1)

1723 cm$^{-1}$ appears in the FTIR spectrum of CFPET-1 or CFPET-2, which results from the stretching vibration peak of C=O. The FTIR measurements indicate that the expected carborane-containing fluorinated polyesters CFPET-1 and CFPET-2 were successfully prepared.

The chemical structures of carborane-containing fluorinated polyesters (CFPET-1 and CFPET-2) were further confirmed by $^1$H-NMR spectroscopy (Fig. 2). As shown in Fig. 2, the fluoropolymer CFPET-1 exhibits three multiple broad peaks: one multiple broad peak at $\delta = 0.81-3.41$ ppm is ascribed to the protons connecting with boron atoms on carborane cage, and the other two at $\delta = 2.74-3.41$ ppm and 2.65−3.31 ppm are ascribed to the protons connecting with −CF$_2$−. These three multiple broad peaks are the characteristic peaks of CDO-1 and LFE, respectively, indicating that the carborane groups have been introduced into the fluorinated polyester. Moreover, a new peak at around $\delta = 3.64$ ppm appears, which associates with the methylene (CH$_2$) protons connecting with −COO− group. The results from $^1$H-NMR measurement confirm the successful synthesis of carborane-containing fluorinated polyesters (CFPET-1). Similar to CFPET-1, CFPET-2 also exhibits the same three multiple broad peaks at $\delta = 0.9-3.42$ ppm, 2.74−3.42 ppm and 2.65−3.31 ppm, which are ascribed to the protons connecting with boron atoms on carborane cage, and the protons connecting with −CF$_2$−, respectively. The methylene protons (CH$_2$, H$_b$–H$_g$) appear around $\delta = 3.83$, 3.62, 2.10, 1.92 and 1.79 ppm. These peaks also confirm that CFPET-2 has been successfully obtained.

## Characterization of Carborane-containing Fluorinated Polyurethanes (CFPU-1 and CFPU-2)

CFPU-1 and CFPU-2 were synthesized by the reaction of HDI trimer with CFPET-1 and CFPET-1, respectively. The FTIR spectrum of CFPU-1 is shown in Fig. 3. For comparison, the spectrum of FPU-1 is also given in Fig. 3. For CFPU-1, the absorption peak at 2601 cm$^{-1}$ is ascribed to the stretching vibration of B−H bonds on the carborane cage. Moreover, the absorption bands around at 3350 cm$^{-1}$ (N−H stretch), 1205 cm$^{-1}$ (−C−O−C) and 1687 cm$^{-1}$ (C=O) are assigned to the urethane linkage, indicating the existence of −NHCOO−. These peaks also confirm the successful synthesis of the expected carborane-containing fluorinated polyurethane CFPU-1. In addition, the −NCO absorption peak of HDI trimer at 2275 cm$^{-1}$ disappears in the spectrum of CFPU-1 and CFPU-2, suggesting that the −NCO groups of HDI trimer have been fully consumed by the condensation polymerization. The spectrum of FPU-1 is similar to that of CFPU-1, but no absorption peak at 2601 cm$^{-1}$ (B−H) on the carborane cage is observed.

## Thermal Stability of CFPU-1 and CFPU-2

To illustrate the influence of carborane group on the thermal property of fluorinated polymer, the thermal properties of carborane-free or containing fluorinated polymers were analyzed using thermal gravimetric analysis (TGA) technique. The TGA curves of carborane-free fluorinated polyester FPET-1 and carborane-containing fluorinated polyesters CFPET-1 and CFPET-2 are shown in Fig. 4. For CFPET-1 and CFPET-2, the obvious weight loss is observed at 225 and 400 °C, and three stages are involved in the
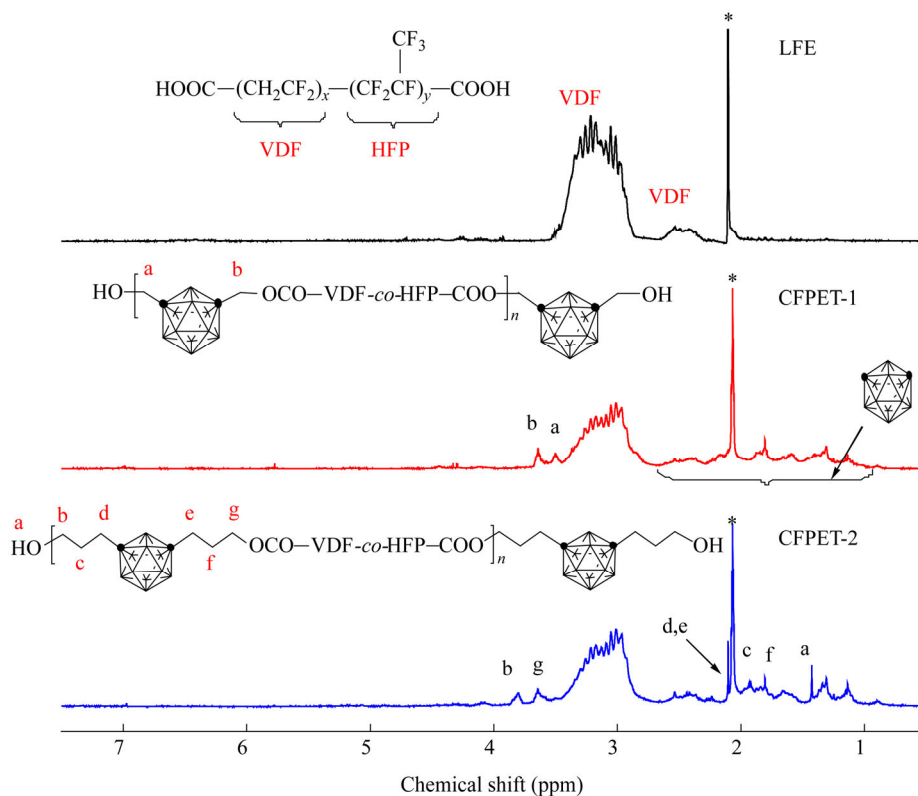


**Fig. 2** $^1$H-NMR spectra of fluorinated polyesters CFPET-1 and CFPET-2 in acetone-d$_6$ (The solvent peaks are marked with asterisks.)
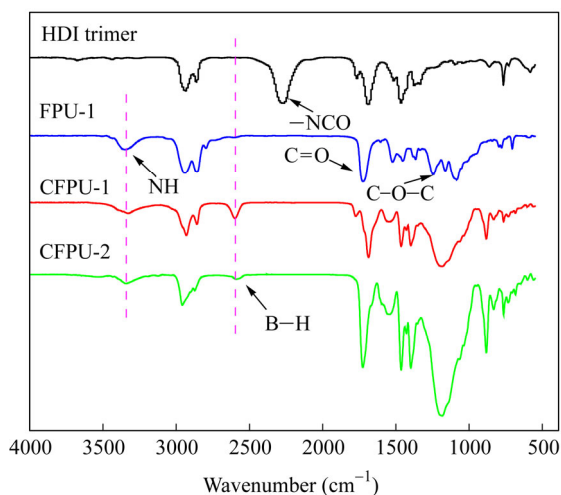
**Fig. 3** FTIR spectra of HDI trimer, FPU-1, CFPU-1 and CFPU-2

process of decomposition in air: (i) room temperature to 225 °C, the weight loss of atmospheric moisture and volatiles, (ii) 225–480 °C, the disintegration of the carborane-free groups, (iii) 480–800 °C, the thermal transformation of carborane group.

In order to evaluate the initial decomposition behavior of polymers, $T_5$ is defined as the temperature at which the resin loses 5% of its original weight, and $T_{10}$ is defined as the temperature at which the resin loses 10% of its original weight. $T_5$ and $T_{10}$ values and the char yields ($Y_c$, at 800 °C) of the three fluorinated polyesters (CFPET-1, CFPET-2 and FPET-1) are summarized in Table 2. Obviously, $T_5$ values for CFPET-1, CFPET-2 and FPET-1 are 285, 229 and 161 °C, respectively. And $T_{10}$ values for them are 365, 328 and 270 °C, respectively. These data indicate that the carborane-containing fluorinated polyesters (CFPET-1 and
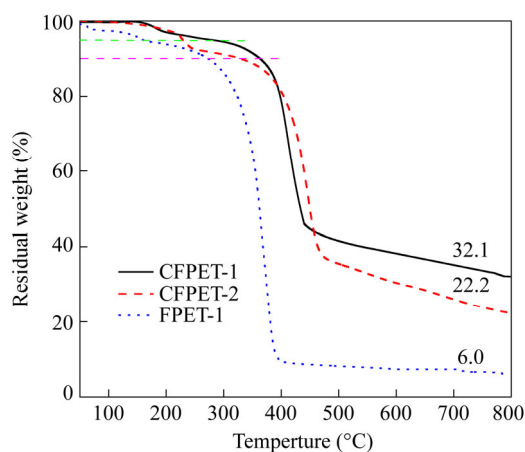
CFPET-2) have higher thermal stability than the carborane-free fluorinated polyester (FPET-1). Meanwhile, the ultimate char yields ($Y_c$) of carborane-containing fluorinated polyesters CFPET-1 and CFPET-2 at 800 °C are 32.1% and 22.2%, respectively. Such data are superior to the carborane-free fluorinated polyester FPET-1 with a low char yield of only 6.0% under the same conditions. The high char yield and decomposition temperature of carborane-containing polyesters indicate that the carborane group can effectively reduce the degradation rate of carborane-containing polyesters. On the other hand, $T_5$ and $T_{10}$ values and the char yield (800 °C) of CFPET-1 are higher than those of CFPET-2. These results demonstrate that the length of carbon chain connecting to the carborane group relates to the thermal resistance of carborane-containing polyester. The shorter the carbon chain lengths are, the better the thermal resistance of carborane-containing polyester will be. The reason may be that the fluorinated polyester with the shorter carbon chain has the stronger steric effect than that with longer carbon chain, which impedes the movement of molecules at high temperature. The results also coincide with our previous work[37].

Figure 5 shows the TGA curves of carborane-containing FPUs (CFPU-1 and CFPU-2) from carborane-containing fluorinated polyesters (CFPET-1 and CFPET-2) and HDI trimer with the molar ratio of NCO/OH = 1/1.5. The TGA curve of carborane-free fluorinated polyurethane FPU-1 is also given for comparison. For CFPU-1 and CFPU-2, there is obvious weight loss in the temperature range of 230–400 °C, and the decomposition process includes three stages: (i) room temperature to 230 °C, the weight loss of small molecules and volatiles, (ii) 230–490 °C, the disintegration of hard segment and soft segment (in particular, the urethane and ester bonds break down, producing $H_2O$ vapor and $CO_2$), (iii) 490–800 °C, the thermal transformation of carborane group. FPU-1 loses its 5% weight at 141 °C, while CFPU-1 loses its 5% weight at 335 °C. $T_{10}$ value of CFPU-1 is 382 °C, which is also much higher than that of FPU-1 as shown in Table 3. Meanwhile, the ultimate char yield ($Y_c$) of CFPU-1 at 800 °C is up to 66.5%, while the $Y_c$ value of FPU-1 is only 34.3%. Also, for CFPU-2, the values of $T_5$, $T_{10}$ and $Y_c$ are all higher than those



**Fig. 4** Thermo-gravimetric curves of FPET-1, CFPET-1 and CFPET-2 in air at a heating rate of 10 K/min

**Table 2** Thermal properties of FPET-1, CFPET-1 and CFPET-2 in air

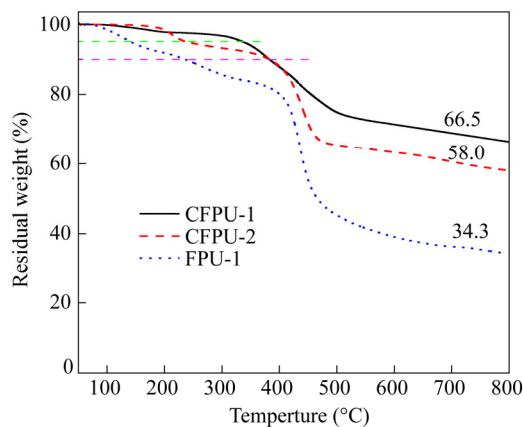| No. | Polyester | $T_5$ (°C) | $T_{10}$ (°C) | $Y_c$ at 800 °C (%) |
|-----|-----------|-----------|--------------|---------------------|
| 1 | FPET-1 | 161 | 270 | 6.0 |
| 2 | CFPET-1 | 285 | 365 | 32.1 |
| 3 | CFPET-2 | 229 | 328 | 22.2 |



**Fig. 5** Thermo-gravimetric curves of FPU-1, CFPU-1 and CFPU-2 in air at a heating rate of 10 K/min

**Table 3**   Thermal properties of FPU-1, CFPU-1 and CFPU-2 in air

| No. | Polyurethane | $T_5$ (°C) | $T_{10}$ (°C) | $Y_c$ at 800 °C (%) |
|-----|-------------|-----------|--------------|---------------------|
| 1 | FPU-1 | 141 | 235 | 34.3 |
| 2 | CFPU-1 | 335 | 382 | 66.5 |
| 3 | CFPU-2 | 238 | 382 | 58.0 |

of FPU-1 under the same conditions. These results indicate that the carborane-containing fluorinated polyurethanes (CFPU-1 and CFPU-2) have higher thermal stability than carborane-free fluorinated polyurethane (FPU-1). On the other hand, $Y_c$ of CFPU-1 is only a little higher than that of CFPU-2 because the $Y_c$ of CFPET-1 is higher than that of CFPET-2. The high char yield and decomposition temperature of the carborane-containing fluorinated polyurethane indicate that the carborane groups can effectively reduce the degradation rate of FPUs and improve the thermal stability at elevated temperatures eventually.
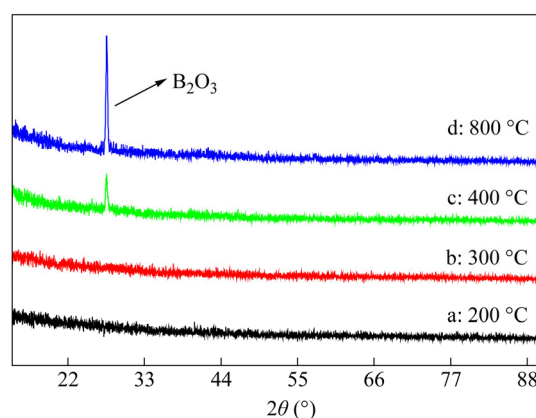
In order to check the structure variation of carborane-containing fluorinated polyurethane at different temperatures, FTIR measurement was performed to analyze the structure of CFPU-1 sample thermally treated at 200, 300, 400 and 800 °C for 2 h in air, respectively. As shown in Fig. 6, CFPU-1 exhibits characteristic absorption peak of B－H bond at 2600 cm$^{-1}$ before thermal treatment, indicating that the carborane cage is intact after curing. After thermally treated at 200 or 300 °C for 2 h, the absorption peak of B－H bond still exists, meaning that the structure of carborane cage has not been destroyed. However, when the temperature is raised to 400 °C, this absorption peak almost disappears, indicating that the B－H bonds on carborane cage have been consumed completely at the elevated temperature. Meanwhile, the absorption peak at 1687 cm$^{-1}$ also disappears at 300 °C, which means that the NHCOO group has been destructed[38]. However, two new broad absorption peaks at 1452 and 640 cm$^{-1}$ appear in the spectrum as the temperature continues to increase, which are ascribed to the stretching vibrations of B－O－B and B－C respectively. The B－O－B and B－C cross-linkages are thermally stable, which improve the char yield and decomposition temperature of the fluorinated
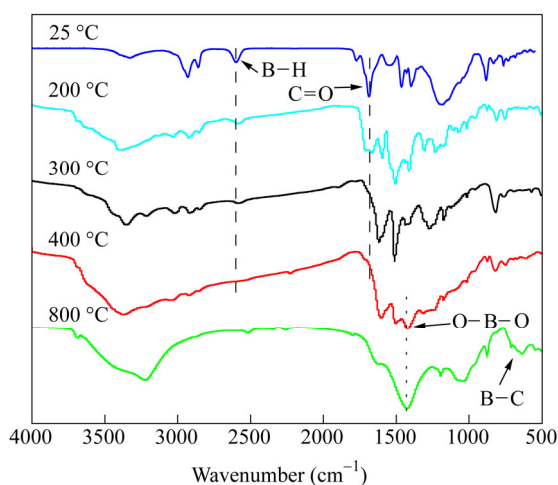
polyurethane[31–35, 37, 38]. Therefore, after oxidation at elevated temperature, these carborane-containing fluorinated polyurethanes (CFPU-1 and CFPU-2) have high char yield and decomposition temperature than those of carborane-free fluorinated polyurethane (FPU-1).

For confirming the structure of oxidized CFPUs, X-ray diffraction (XRD) technique was utilized to study the XRD patterns of CFPU-1 that were thermally treated at 200, 300, 400 and 800 °C for 2.5 h under air. When the CFPU-1 sample was thermally treated at 200 and 300 °C, no sharp crystalline peaks are observed, and the CFPU-1 sample exhibits amorphous structure (Figs. 7a and 7b). When the thermal treatment temperature increased to 400 and 800 °C, the Bragg reflection at $2\theta$ of 27.8° (Figs. 7c and 7d) was attributed to crystalline diffraction peaks of $B_2O_3$[32, 39, 40]. These XRD patterns indicate that the structure of the carborane cage had not been destroyed yet when the thermal treatment temperature was below 300 °C. However, when the temperature was elevated to 400 °C, the structure of carborane cage was destroyed and a more stable $B_2O_3$ was formed. The above results coincide with the TGA curve of CFPU-1 (Fig. 5) and the FTIR spectra of CFPU-1 after thermal treatment at different temperatures (Fig. 6). When the temperature was lower than 400 °C, the carborane groups had not been pyrolyzed; only the carborane-free fragments were disintegrated into small molecules, resulting in a slow degradation process of CFPU-1. When the temperature was elevated to 400 °C, the carborane-free fragments were disintegrated eventually, giving rise to quick loss of the weight of CFPU-1. However, the trend of weight loss of CFPU-1 was put off because of the existence of carborane cages. Although the carborane cages underwent pyrolysis at 400 °C, they could form more compact oxidation $B_2O_3$ layer, which was stable even at 800 °C. Therefore, the CFPU-1 has a high char yield at elevated temperature.

SEM images of cured FPU-1 and CFPU-1 films before and after thermal treatment are presented in Fig. 8. Before thermal treatment, the surfaces of cured FPU-1 and CFPU-1 films are smooth as shown in Figs. 8(a) and 8(b). However, after thermal treatment, the surface of cured FPU-1 film becomes rough (Fig. 8c), while the surface of cured CFPU-1 film is



**Fig. 6**  FTIR spectra of carborane-containing fluorinated polyurethane (CFPU-1) after thermal treatment at different temperatures for 2 h



**Fig. 7**  XRD patterns of carborane-containing fluorinated polyurethane (CFPU-1) after thermal treatment at different temperatures for 2.5 h
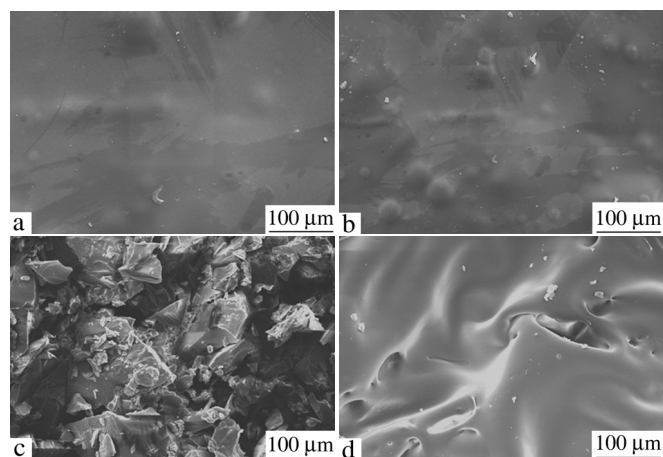
**Fig. 8** SEM images of cured FPU-1 (a, c) and CFPU-1 (b, d) films before and after thermal treatment at 600 °C for 2 h

still relatively smooth except for some wrinkles (Fig. 8d). These images also demonstrate that the incorporation of carborane groups can improve the stability of the fluorinated polyurethane at high temperature. This may be attributed to that a compact oxidized B—C or a $B_2O_3$ cross-linkage layer forms on the surface of the CFPU film at high temperature during the oxidation process of carborane cage, and the formed strong B—C or $B_2O_3$ cross-linkage protective layer is thermally stable, which postpones the thermal decomposition of fluorinated polyurethane. The SEM image is corresponding to the result of XRD. Therefore, the surface of the cured CFPU-1 film is more intact than that of the cured FPU-1 film.

**Flame Retardant Properties of CFPU-1 and CFPU-2**

Polymers containing B atoms usually possess excellent flame retardant property[41–43]. In order to explore the flame retardant properties of CFPU-1 and CFPU-2, the dynamic combustion performance of them was studied. We measured the values of the heat release rate (HRR), total heat release (THR) and limited oxygen index (LOI) of the CFPU-1 and CFPU-2. Among them, PHRR is defined as the maximum value of HRR, and LOI is taken as an indicator to evaluate the polymer's flame retardancy. For comparison, the corresponding values of FPU-1 were also provided. As shown in Figs. 9 and 10, the fluorinated polyurethanes containing carborane (CFPU-1 and CFPU-2) have lower PHRR and THR values and higher LOI values than those of carborane-free fluorinated polyurethane (FPU-1). The PHRR and THR values of CFPU-1 are only 256.7 kW/m² and 6.9 MJ/m², respectively, whereas, the PHRR and THR values of FPU-1 reach up to 348.2 kW/m² and 9.2 MJ/m², respectively. Besides, LOI of CFPU-1 and CFPU-2 is 36% and 35% while FPU-1 is only 26%. All above data indicate that fluorinated polyurethanes containing carborane possess better flame retardant property than carborane-free FPU. When the fluorinated polyurethane polymers containing carborane (CFPU-1 and CFPU-2) combusted, a compact oxidation B—C or $B_2O_3$ cross-linkage layer formed on the surface of the CFPU film. It could prevent the generated combustible gases from transferring to the surface of materials, and so oxygen pathway was cut off. At the same time, the heat radiation for polymer material also reduced.
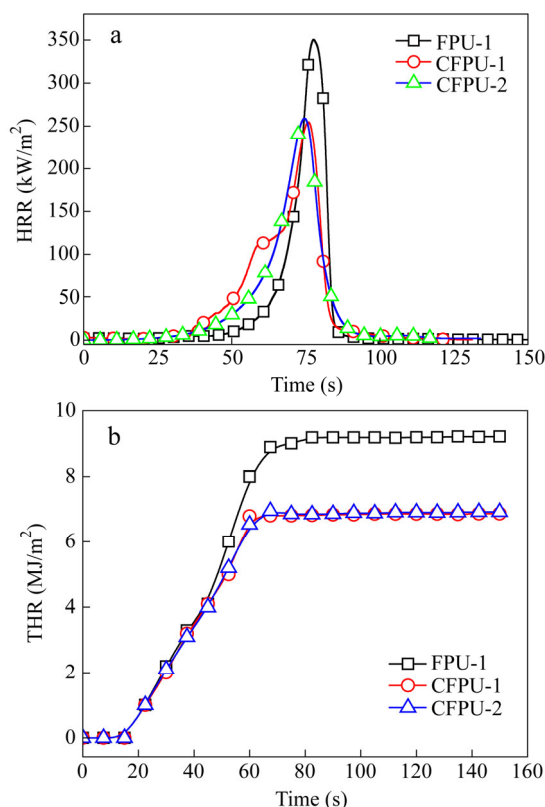


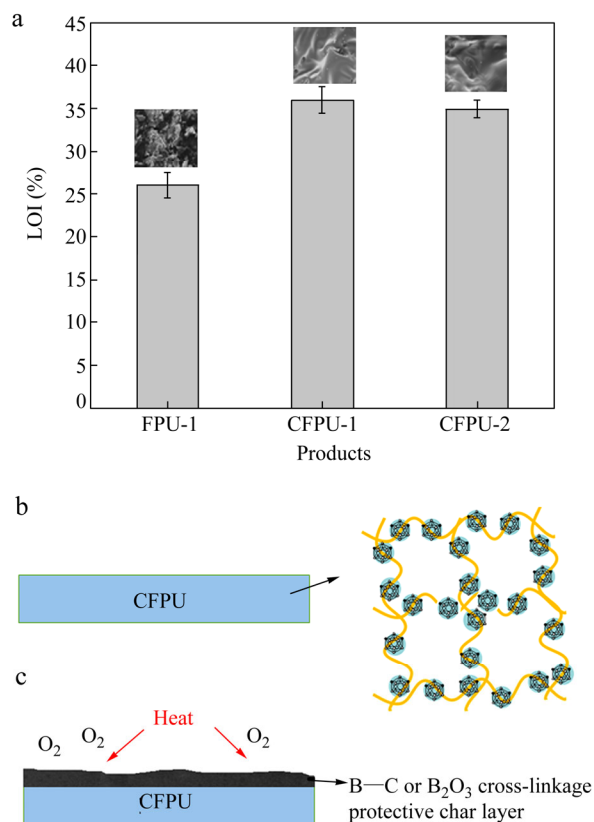**Fig. 9** HRR (a) and THR (b) of FPU-1, CFPU-1 and CFPU-2



**Fig. 10** LOI of FPU-1, CFPU-1 and CFPU-2 (a) and schematic representations of cured CFPU films before and after thermal treatment (b, c)

Therefore, the CFPU-1 and CFPU-2 have lower PHRR, THR and higher LOI values than those of FPU-1. The stability of carborane group makes CFPUs have higher char yield, which are corresponding to the TGA results.

**Surface Properties of CFPU-1 and FPU-1**

The hydrophobicity and lipophobicity of CFPU-1 and FPU-1 were assessed by measuring the static contact angle (CA) by using the sessile drop method (Fig. 11). It can be found that CAs of water and ethylene glycol of the cured CFPU-1 films
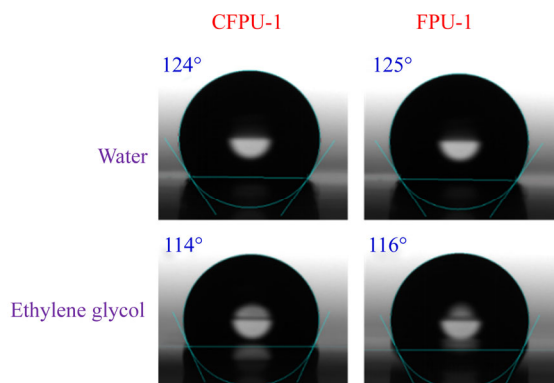


**Fig. 11**  CAs of water and ethylene glycol of the cured CFPU-1 and FPU-1 films

are 124° and 114°, respectively, which are all slightly lower than those of FPU-1 films. The CAs of water and ethylene glycol of the cured FPU-1 films are 125° and 116°, respectively. This means that the introduction of carborane groups into the fluorinated polyurethane almost had no influence on the surface properties of fluorinated polyurethane.

**Chemical Resistance of CFPU-1, FPU-1 and OPU Films**

Generally, carborane has a good chemical resistance[29–32]. In order to verify whether the carborane could enhance the chemical resistance of the fluorinated polyurethane or not (such as oil resistance, organic solvent-resistance and acid-alkali resistance), the cured carborane-free FPU-1 and carborane-containing CFPU-1 films were prepared according to ASTM D471-02, and then immersed into four different solutions: Jet aircraft oil, cyclohexane, 37% HCl and 45% NaOH, respectively. Figure 12 shows the weight change curves of the cured FPU-1 and CFPU-1 films at different time at room temperature. The curves of an ordinary carborane-free and fluorine-free polyurethane OPU are also given for comparison. As shown in Fig. 12, the weight changes of OPU in the four media are about 30%–60% after 168 h, so the chemical resistance of the OPU is not satisfactory. However, the weight changes of FPU-1 and CFPU-1 in Jet aircraft oil and cyclohexane are
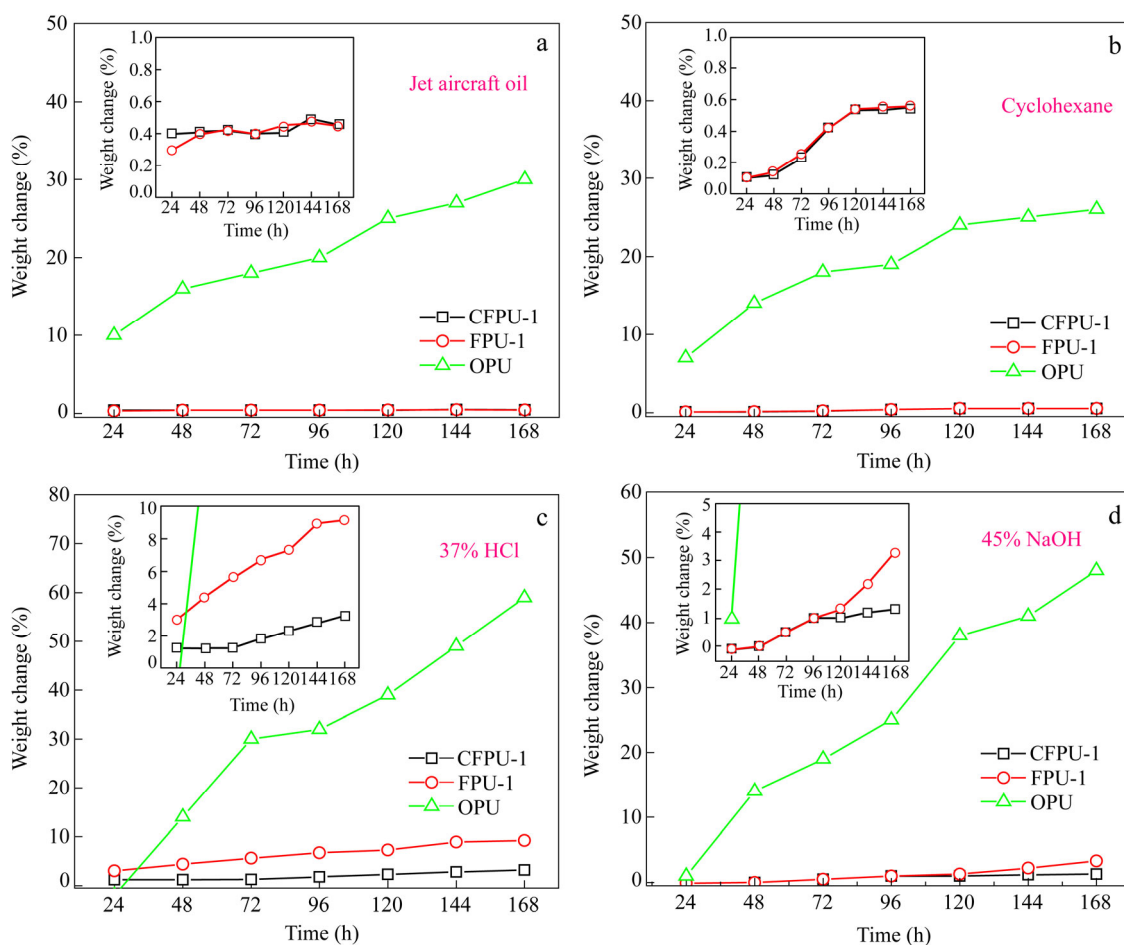


**Fig. 12**  Weight change of CFPU-1, FPU-1 and OPU films in four different solutions: Jet aircraft oil (a), cyclohexane (b), 37% HCl (c) and 45% NaOH (d) at different time at room temperature (The insets show the amplified corresponding graphs.)

lower than 1%, indicating that the cured fluoropolymers FPU-1 and CFPU-1 have good oil and organic solvent resistance. In addition, the weight changes of CFPU-1 in 37% HCl and 45% NaOH solution are much smaller than those of FPU-1. Obviously, fluorinated polyurethane containing carborane group has better organic solvent, acid and alkali resistance.

In order to understand the mechanism of chemical resistance, the micro-surfaces of cured FPU-1 and CFPU-1 films before and after immersed into organic solvent and acid solution (Jet aircraft oil and 37% HCl) for 168 h were examined by scanning electron microscopy (SEM, Fig. 13). It can be seen from Figs. 13(a) and 13(b) that the cured FPU-1 and CFPU-1 films without soaking in organic solvent or acid solution show smooth surfaces. After immersed into Jet aircraft oil or 37% HCl solution, the surface of cured CFPU-1 film is still smooth without obvious change (Figs. 13b1 and 13b2), while the surface of cured FPU-1 film becomes rough and uneven (Figs. 13a1 and 13a2) and the traces of corroded by solvents are obvious. Obviously, the surface of CFPU-1 (Fig. 13b) has more compacted structure than those of FPU-1. This compacted structure may be the primary reason of excellent solvent resistance of CFPU-1, which can reduce the corrosion rate of cyclohexane, HCl, and NaOH, *etc*. The structural characteristic of carborane group may be the main factor that makes the structure of CFPU-1 more compact[44–46]. The charge distribution of carborane and closed polyhedral structure of the "boron-cage" have strong electron-deficiency, shorter bond length of adjacent groups and increased degree of ionization, which cause the structure of CFPU-1 more densified and compact. On the other hand, the carborane group with large volume has a steric effect[47–50], which limits the movement of adjacent chain segment when it is immersed in solvent. Consequently, the cured CFPU-1 films have better chemical resistance than

the cured FPU-1 films.

**Mechanical Properties of CFPU-1, FPU-1 and OPU Films**
In order to further verify the mechanical properties of CFPU-1 films in harsh environment, such as extremely high concentrations of acid-alkali corrosion and high temperature, the CFPU-1 films were immersed into organic solvent and acid solution (Jet aircraft oil and 37% HCl) and compared with FPU-1 and OPU films at the same time. The tensile strength and elongation at break were examined. The results are shown in Fig. 14. Meanwhile, the tensile strength, elongation at break and Shore A hardness of the non-immersed films at room temperature were also examined (Table 4). With time increasing, the tensile strength of FPU-1, CFPU-1 and OPU films decreased gradually, and their elongation at break all increased. Nevertheless, the changes of the two mechanical parameters of fluorinated polyurethane films of FPU-1 and CFPU-1 are smaller than that of fluoride-free polyurethane (OPU). It is worth noting that the cured CFPU-1 films have the highest tensile strength and the lowest of elongation at break among the three cured films, no matter whether or not these cured films were immersed into the media. The better mechanical property of CFPU-1 is attributed to the high rigidity of carborane in the main chain as illustrated in Fig. 15. When CFPU-1 suffered external forces, the strong electron-deficiency of carborane made it more densified and compact. The steric effect of huge carborane cage caused the chain movement difficult, and the large size of the cage structure also had steric effect on the adjacent groups. It is obvious that the mechanical properties of FPU can be improved by introducing the carborane groups into the main chain of polyurethane in acid media.

High temperature is one of the main reasons for the degradation of polyurethane materials. In order to evaluate the mechanical properties of carborane-containing fluorinated polyurethane under high temperature, the tensile strength
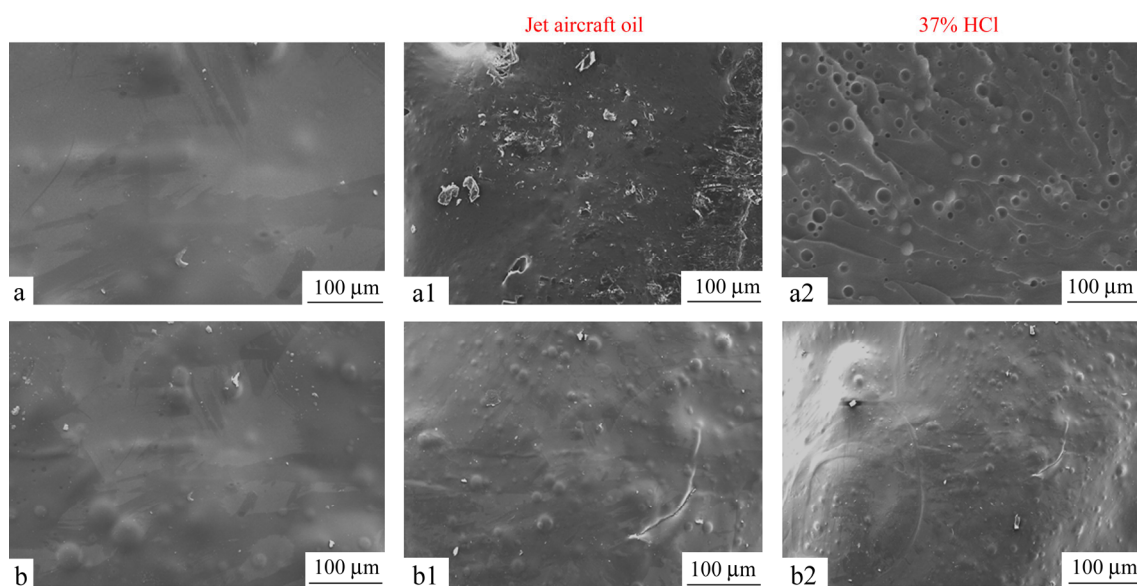


**Fig. 13**   SEM images of cured FPU-1 (a, a1, a2) and CFPU-1 (b, b1, b2) films before (a, b) and after immersed into Jet aircraft oil (a1, b1) and 37% HCl (a2, b2)
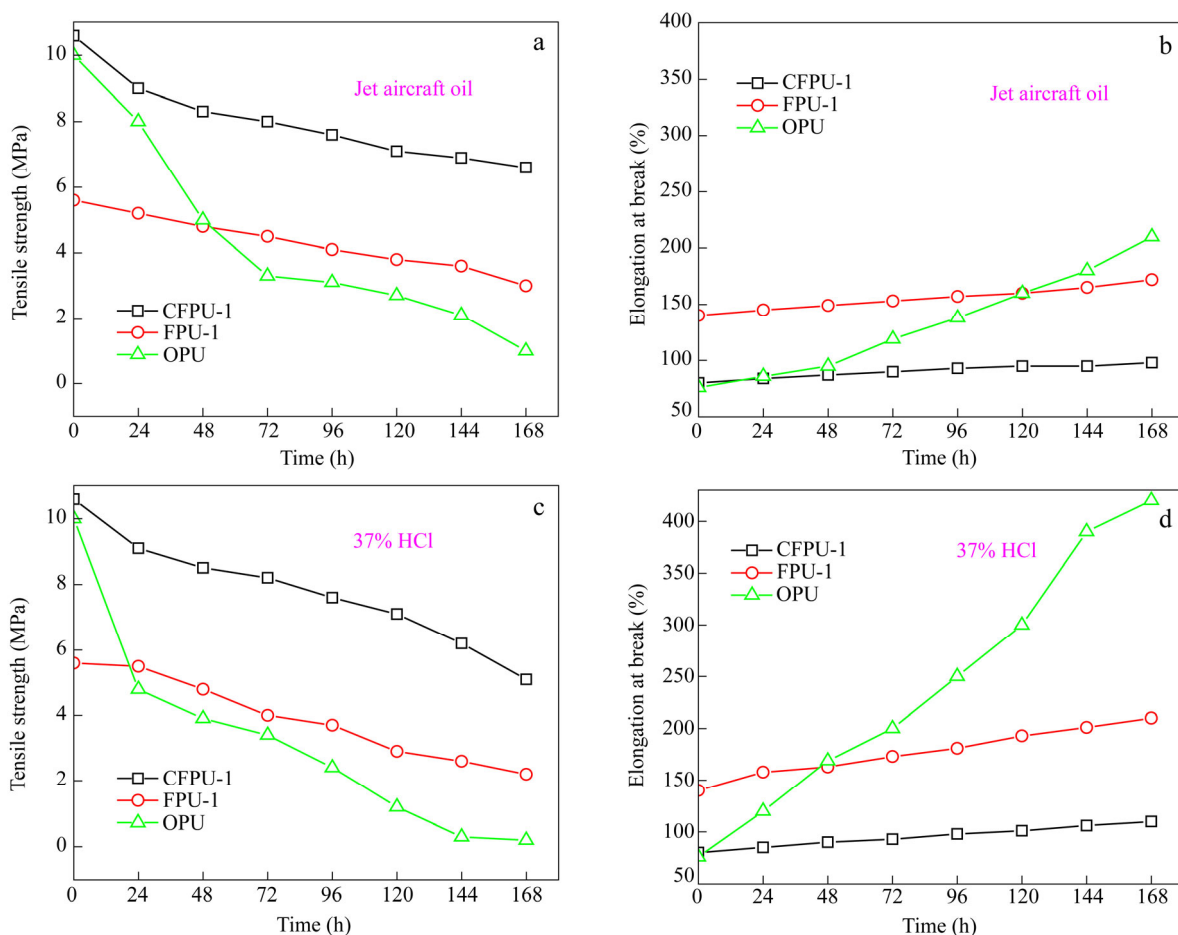
**Fig. 14** Mechanical properties of OPU, FPU-1 and CFPU-1 after immersed into Jet aircraft oil (a, b) and 37% HCl (c, d) at room temperature

**Table 4** Mechanical properties of the non-immersed OPU, FPU-1 and CFPU-1 films at room temperature

| Properties | FPU-1 | CFPU-1 | OPU |
|---|---|---|---|
| Tensile strength (MPa) | 5.6 | 10.61 | 10 |
| Elongation at break (%) | 140 | 81 | 76 |
| Shore A hardness | 50 | 55 | 56 |

and impact strength of CFPU-1 were tested at different temperatures; FPU-1 and OPU were also tested for comparison. Their curves exhibit the similar variation trend to those of solvent resistance as shown in Fig. 16. With temperature increasing, the tensile strength of FPU-1,

CFPU-1 and OPU films decreases gradually; the value and change rate of the mechanical parameter of three polyurethane polymers is in the order of OPU > FPU-1 > CFPU-1. Moreover, CFPU-1 has the highest value of impact strength above 400 °C; even at 600 °C, carborane-containing fluorinated polyurethane (CFPU-1) still has a bit of toughness. All above results are attributed to the compacted structure of product, and the steric effect of carborane in the main chain. Its "super aromatic" cage structure plays the role of "energy groove", which makes the whole molecule stable. Even at high temperature, the large size of the cage structure can
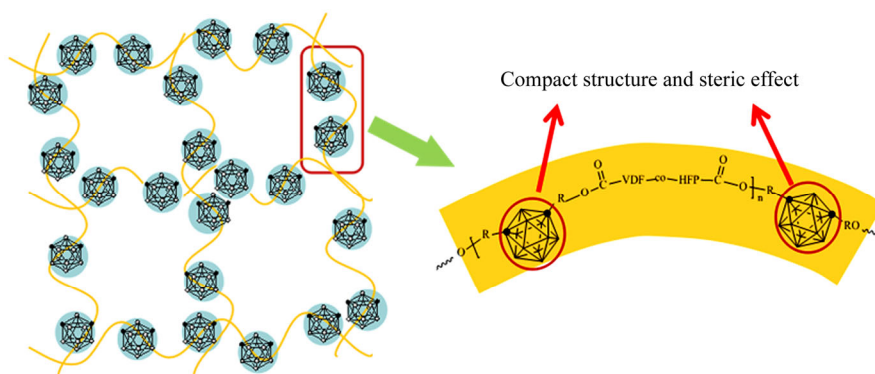


**Fig. 15** Schematic representation of cured CFPU films with good mechanical properties
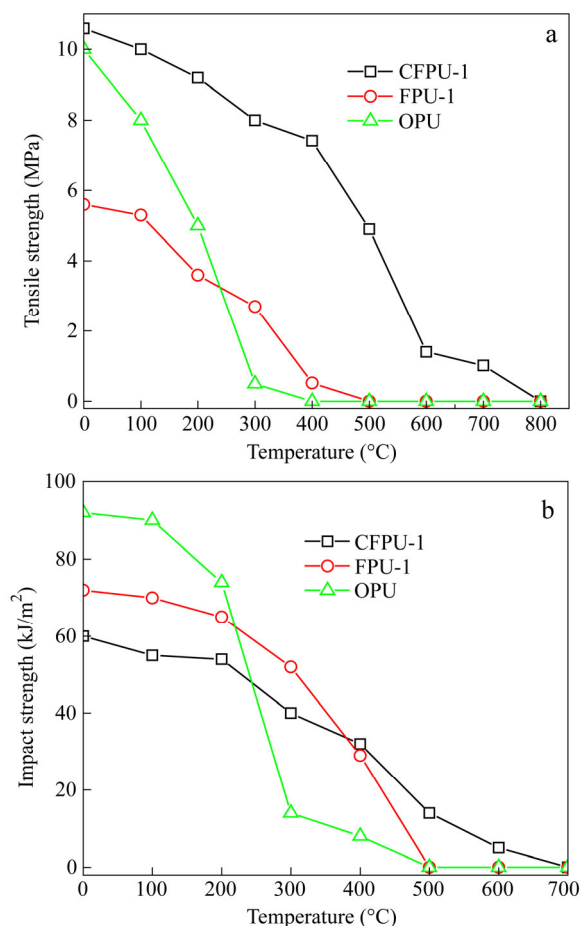
**Fig. 16** Tensile strength (a) and impact strength (b) of OPU, FPU-1 and CFPU-1 at different temperatures

slow down the speed of thermal degradation. And the formed strong protective char layer consisting of B—O—B and B—C cross-linkages at high temperature is helpful to improve the mechanical properties of the material.

## CONCLUSIONS

In this work, two carborane-containing fluorinated polyurethanes (CFPU-1 and CFPU-2) were prepared by reacting the carborane-containing polyesters (CFPET-1 and CFPET-2) with HDI trimer at room temperature. TGA tests manifested that the introduction of carborane groups into the main chain of fluorinated polyurethane endowed the obtained fluorinated polyurethane with excellent thermal stability. The thermal decomposition of carborane fluorinated polyurethane (CFPU) increased by 190 °C compared with that of the carborane-free fluorinated polyurethane (FPU). Even at 800 °C, CFPU still showed higher char yield (66.5%) than that of FPU (34.3%). The carborane-containing fluorinated polyurethanes exhibited good acid-alkali resistance. The obtained carborane-containing fluorinated polyurethanes also displayed excellent mechanical property, even after the cured films being immersed into Jet aircraft oil or 37% HCl for 168 h or at high temperature (700 °C). The structural characteristics of carborane group and the compacted structure of the

product effectively improve the thermal stability, mechanical properties, solvent and acid-alkali resistance of the carborane-free fluorinated polyurethane. They can be widely used as the raw materials to prepare the high-temperature resistant coatings or adhesives for automotive engines, aircraft and other equipment working in high-temperature or high concentrations of acid-alkali environment, for example the sealant of fuel tank in a car or plane, the high-temperature resistant coatings on the surface of aircraft. Under these harsh environments, the good thermal stability, excellent chemical resistance and mechanical properties are capable of keeping fluorinated polyurethane stable and expanding their service lives.

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